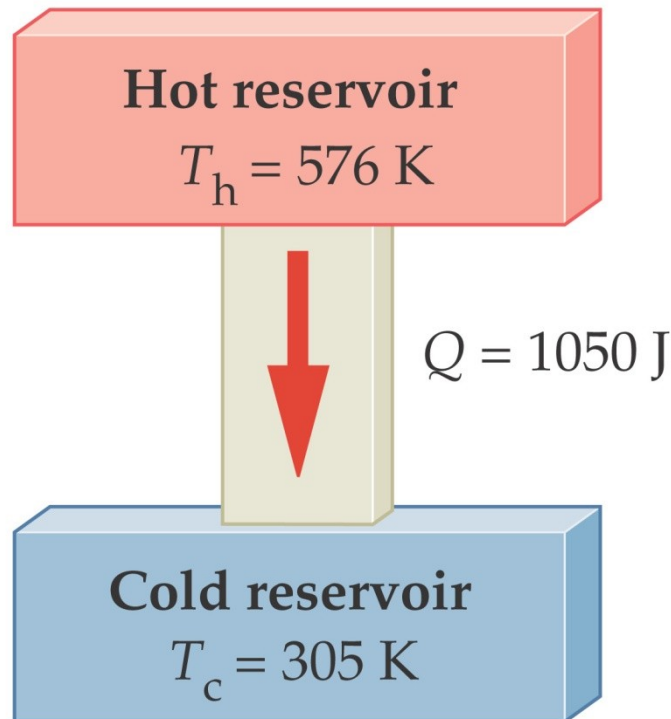


Thermodynamics relates **heat** and
motion

thermo = **heat**

dynamics = **motion**

The Laws of Thermodynamics



First Statement of the Second Law of Thermodynamics

The first statement of the second law is a statement from common experience.

- 1. When two objects, one hot and the other cold, come into contact, heat energy will be transferred from the system at **higher temperature** to the system at **lower temperature**, but not vice versa.**
- 2. The 1st law of thermodynamics does not clarify this, that is why we have the 2nd Law**

Second Statement of the Second Law: Heat Engines

A ***heat engine*** is a device that is capable of changing **thermal energy** (Q_H), also known as the **input heat** or heat of combustion of the fuel, into **useful work** (W).

The second law of thermodynamics

- Thomson's formulation (1851):
- No set of processes can be reduced only to the conversion of heat into work, while the conversion of work into heat can be the only result of the process.

Carnot's question

How much work can be produced from a given quantity of heat?

“...whether the **motive power of heat** is unbounded, whether the possible improvements in steam-engines have an assignable **limit**, a limit which the nature of things will not allow to be passed by any means whatever...”

Modern translations

Motive power: work

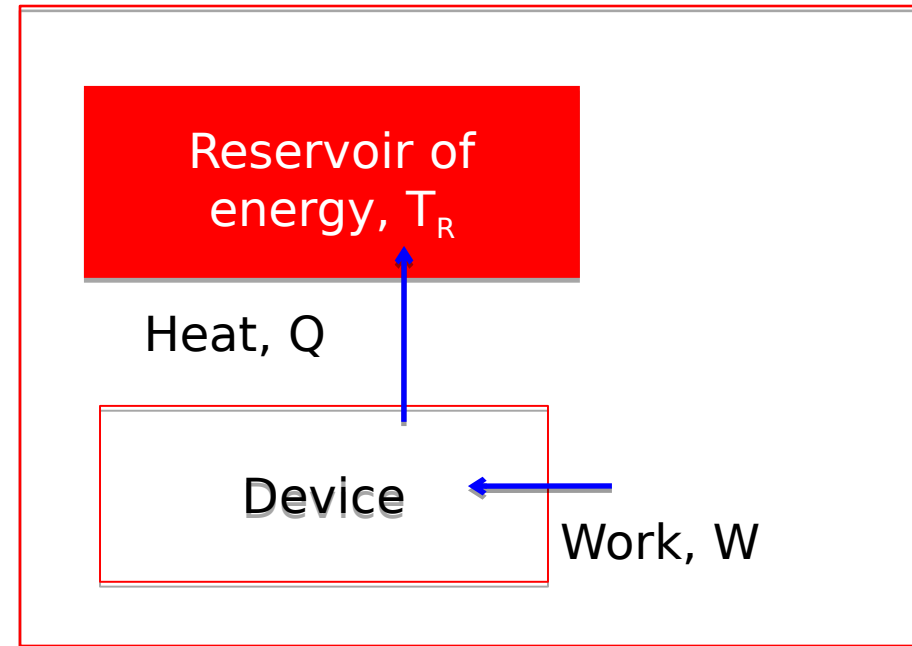
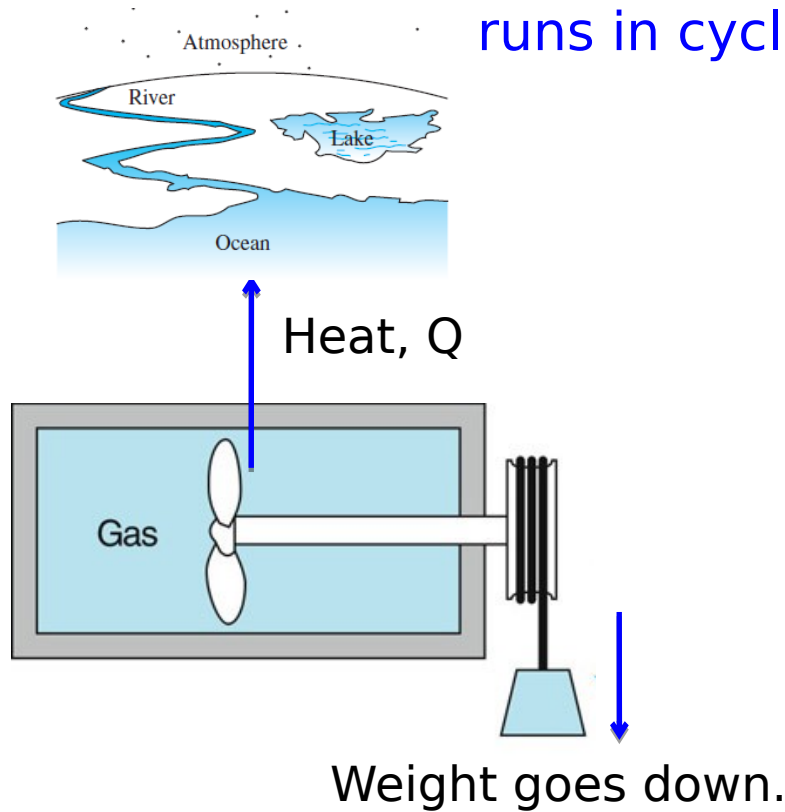
Motive power of heat: work produced by heat

Limit: Carnot limit, Carnot efficiency

Thermodynamics permits heater

runs in cycle to convert work to heat

Isolated system



Device runs in cycle: $\Delta U_{\text{device}} = 0, \Delta S_{\text{device}} = 0$

Isolated system conserves
energy:

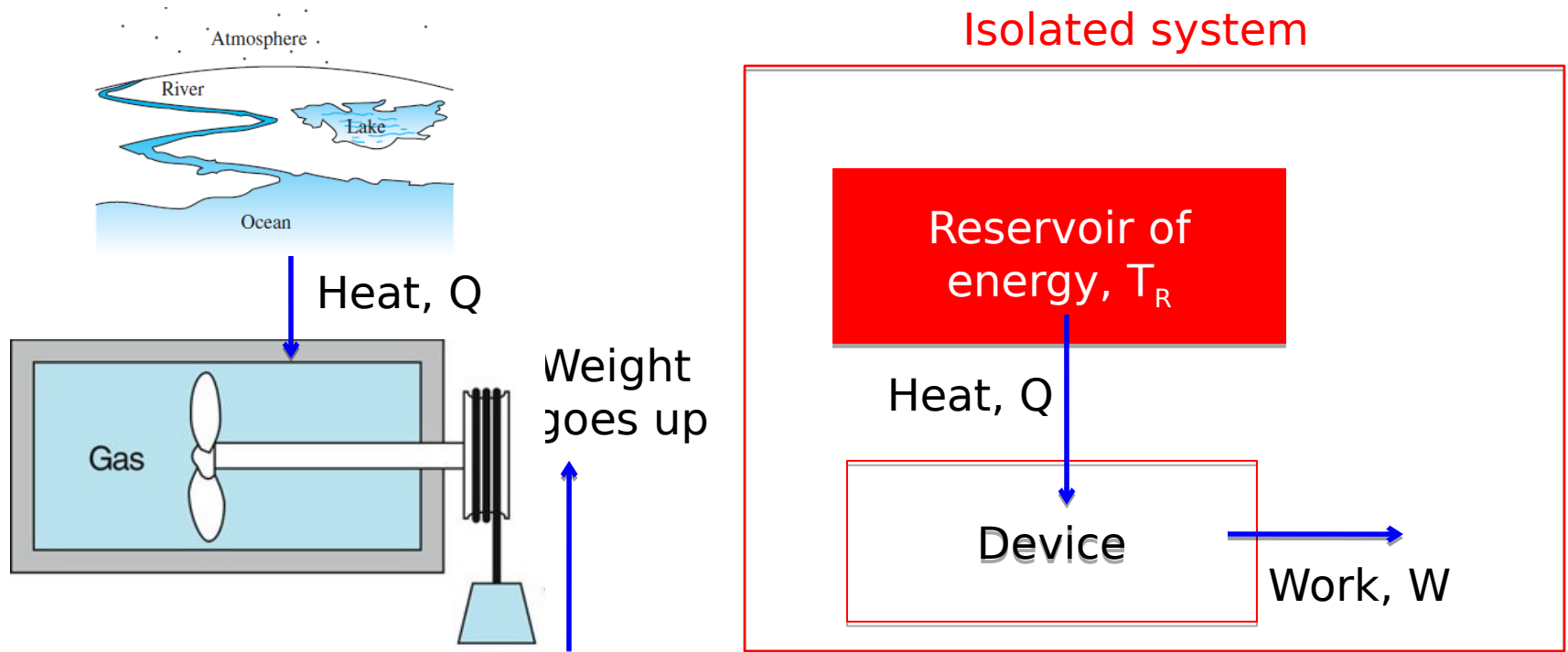
$$Q = W$$

$$\frac{Q}{T_R} \geq 0$$

Isolated system generates

Thermodynamics **forbids** perpetual motion of the second kind

a device runs in cycle to produce work by receiving heat from a **single reservoir**



Device runs in cycle: $\Delta U_{\text{device}} = 0, \Delta S_{\text{device}} = 0$

Isolated system conserves
energy:

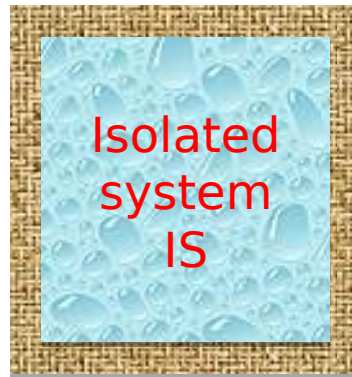
$$Q = W$$

$$-\frac{Q}{T_R} \geq 0$$

Isolated system generates

Isolated system

When confused, isolate.



Isolated system **conserves mass** over time:

$$\frac{dm_{IS}}{dt} = 0$$

Isolated system **conserves energy** over time:

$$\frac{dE_{IS}}{dt} = 0$$

Isolated system **generates entropy** over time:

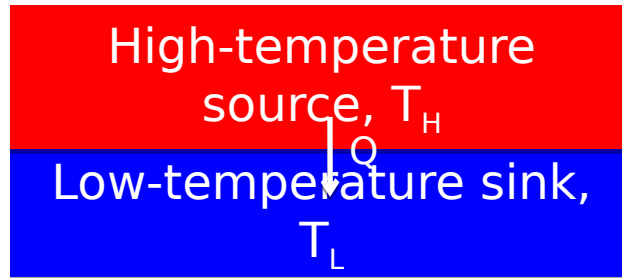
$$\frac{dS_{IS}}{dt} \geq 0$$

$$\frac{dS_{IS}}{dt} \begin{cases} > 0, \text{ irreversible process} \\ = 0, \text{ reversible process} \\ < 0, \text{ impossible process} \end{cases}$$

Define more **words**:

Carnot's remarks

1. “Wherever there exists a difference of temperature, motive power can be produced.”
2. To maximize motive power, “contact (between bodies of different temperatures) should be avoided as much as possible”



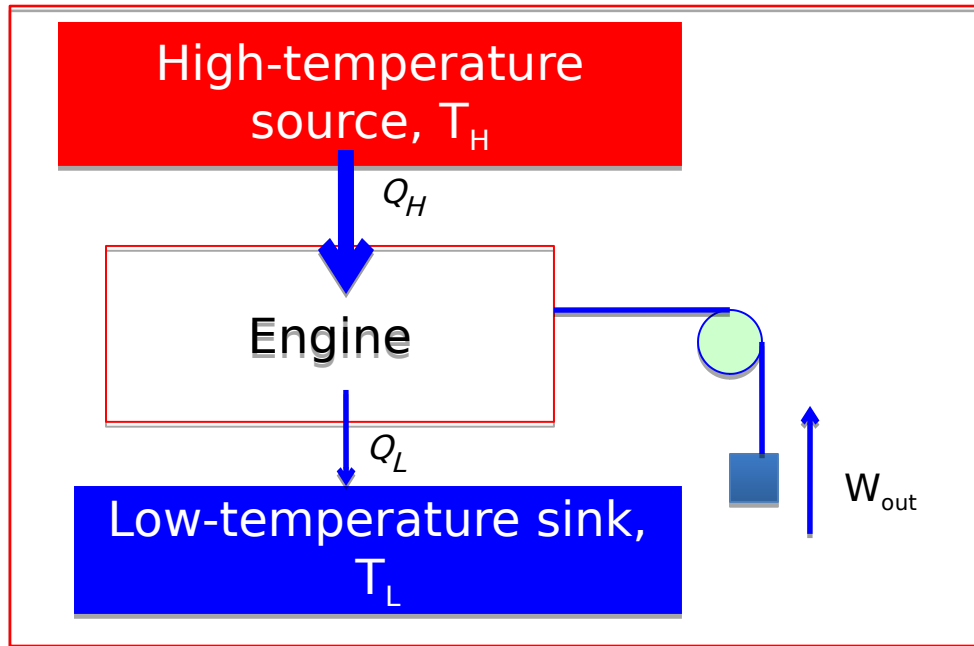
Thermal contact of reservoirs of different temperatures generates entropy, and does no work.

$$S_{gen} = \frac{Q}{T_L} - \frac{Q}{T_H}$$

Two reservoirs

For an engine running in cycle to convert heat to work, a single reservoir will not do; we need **reservoirs of different temperatures.**

Isolated system of 4 parts



$$\Delta U_H = -Q_H, \quad \Delta S_H = -\frac{Q_H}{T_H}$$

$$\Delta U_{engine} = 0, \quad \Delta S_{engine} = 0$$

$$\Delta U_{weight} = W_{out}, \quad \Delta S_{weight} = 0$$

$$\Delta U_L = Q_L, \quad \Delta S_L = \frac{Q_L}{T_L}$$

Isolated system conserves energy

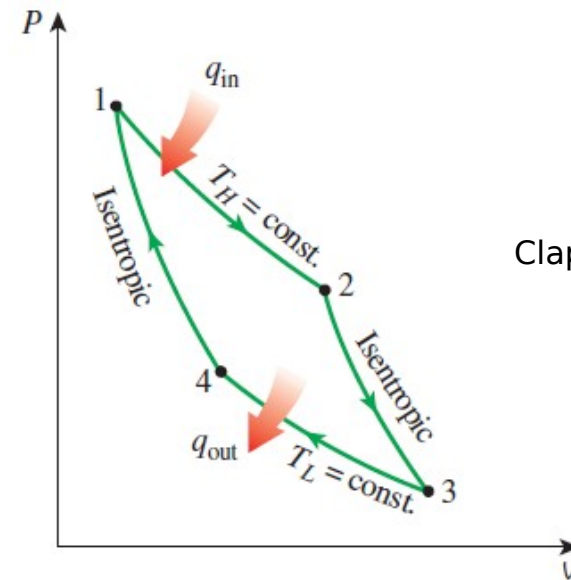
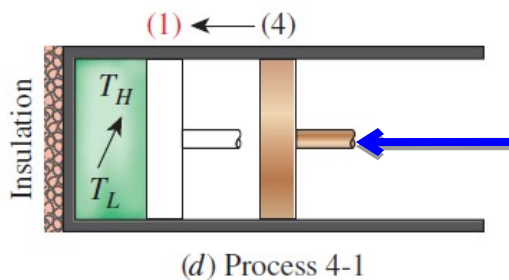
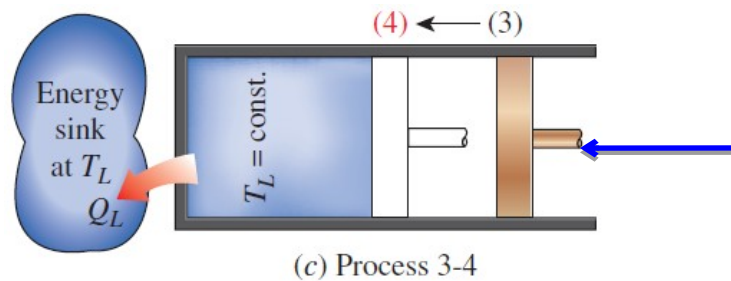
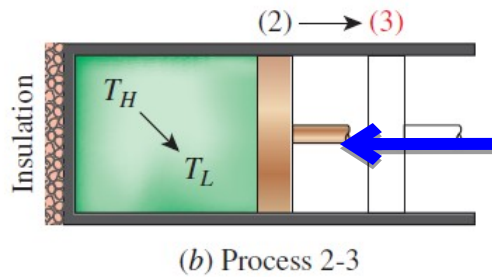
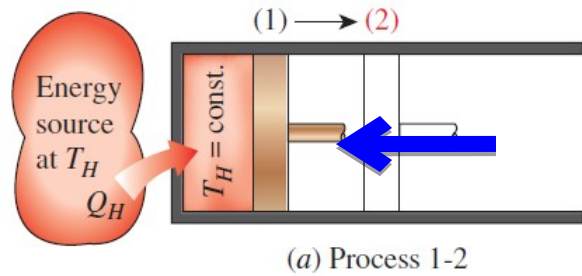
$$W_{out} - Q_H + Q_L + 0 = 0$$

isolated system generates

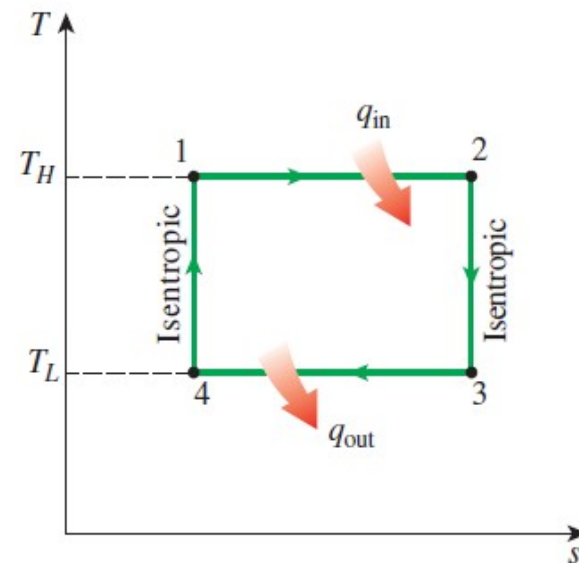
$$0 - \frac{Q_H}{T_H} + \frac{Q_L}{T_L} + 0 \geq 0$$

Carnot cycle

Carnot (1824)



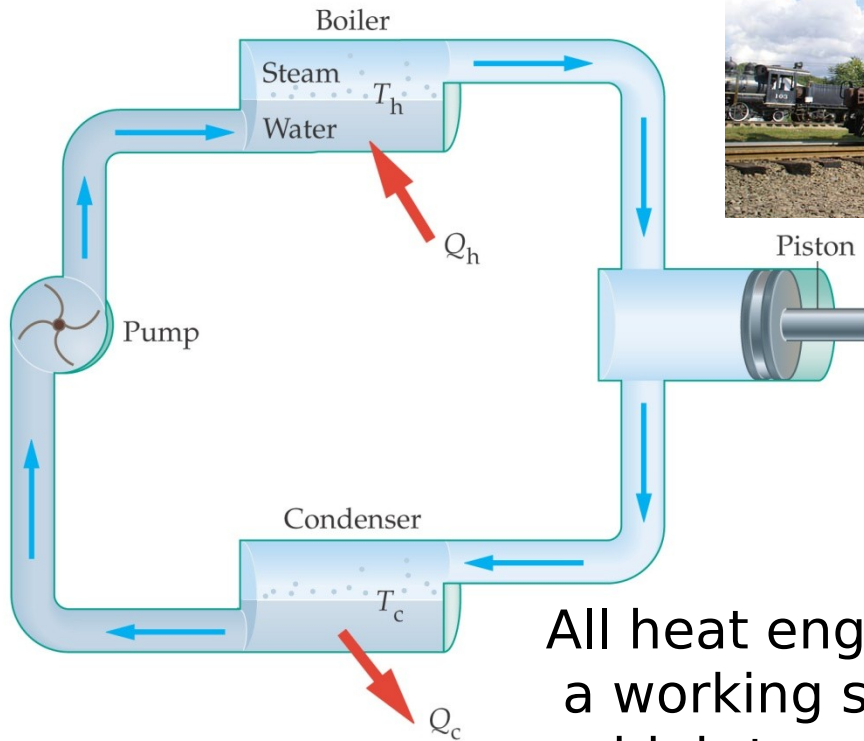
Clapeyron (1834)



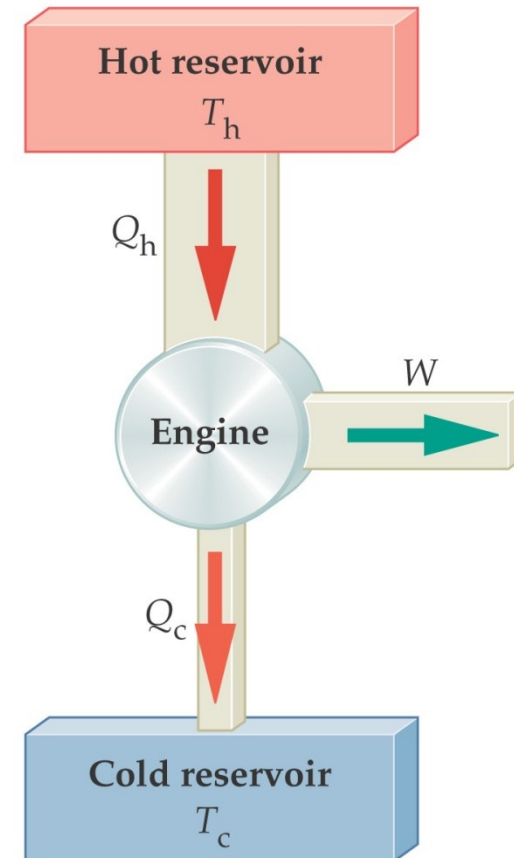
Gibbs (1873)

Heat Engines

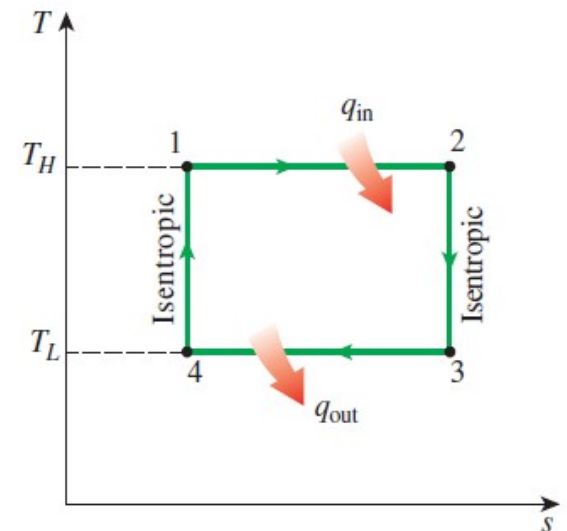
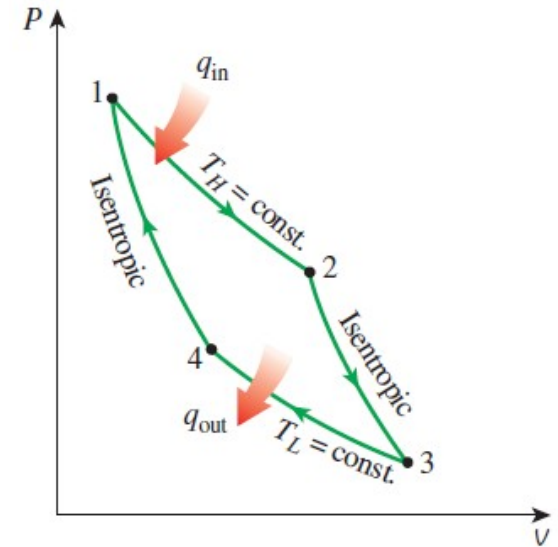
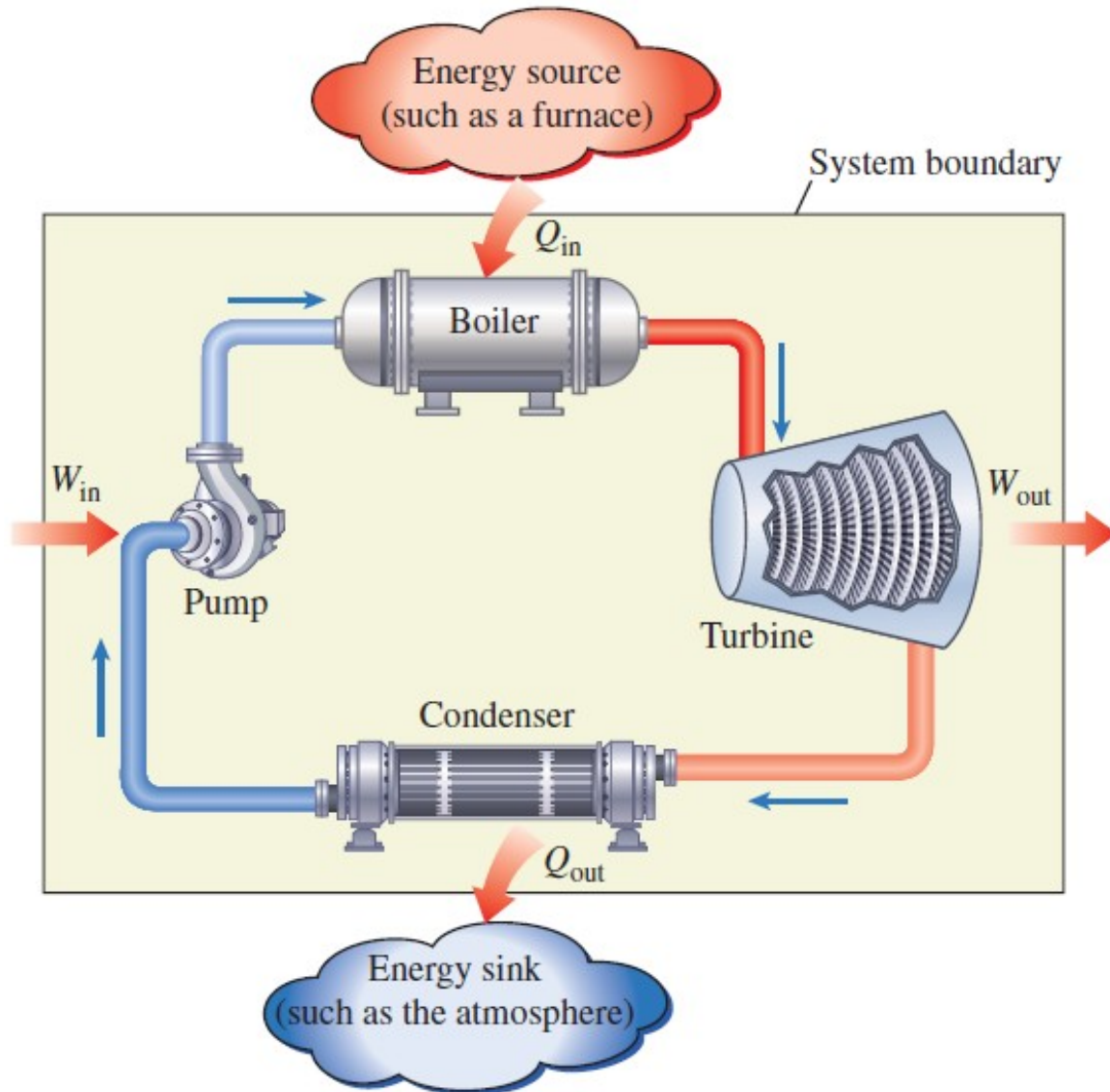
A heat engine is a device that converts heat into work. A classic example is the steam engine. Fuel heats the water; the vapor expands and does work against the piston; the vapor condenses back into water again and the cycle repeats.



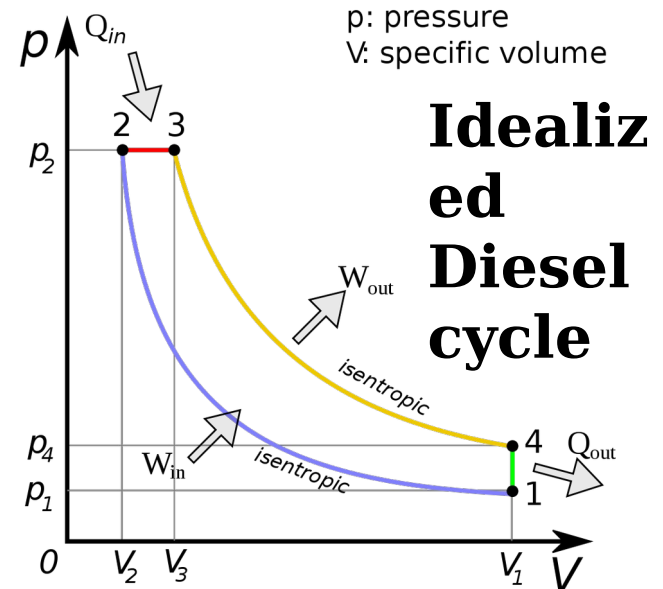
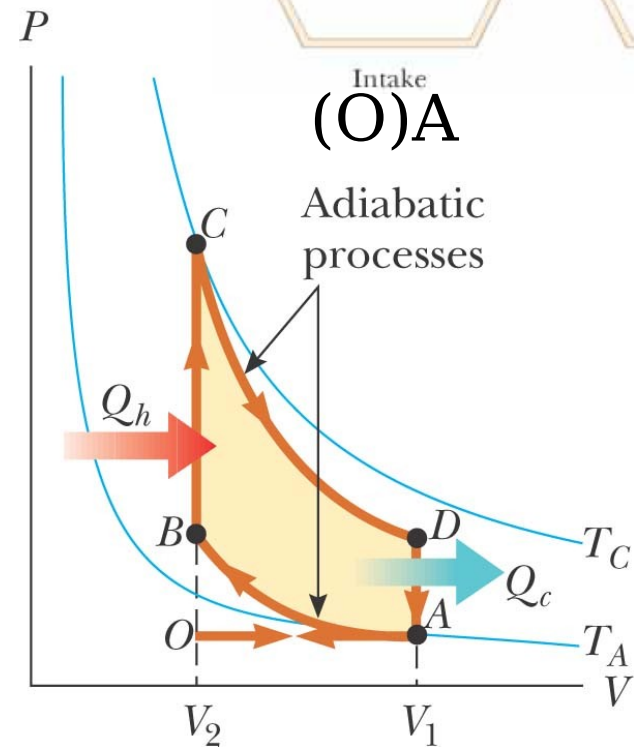
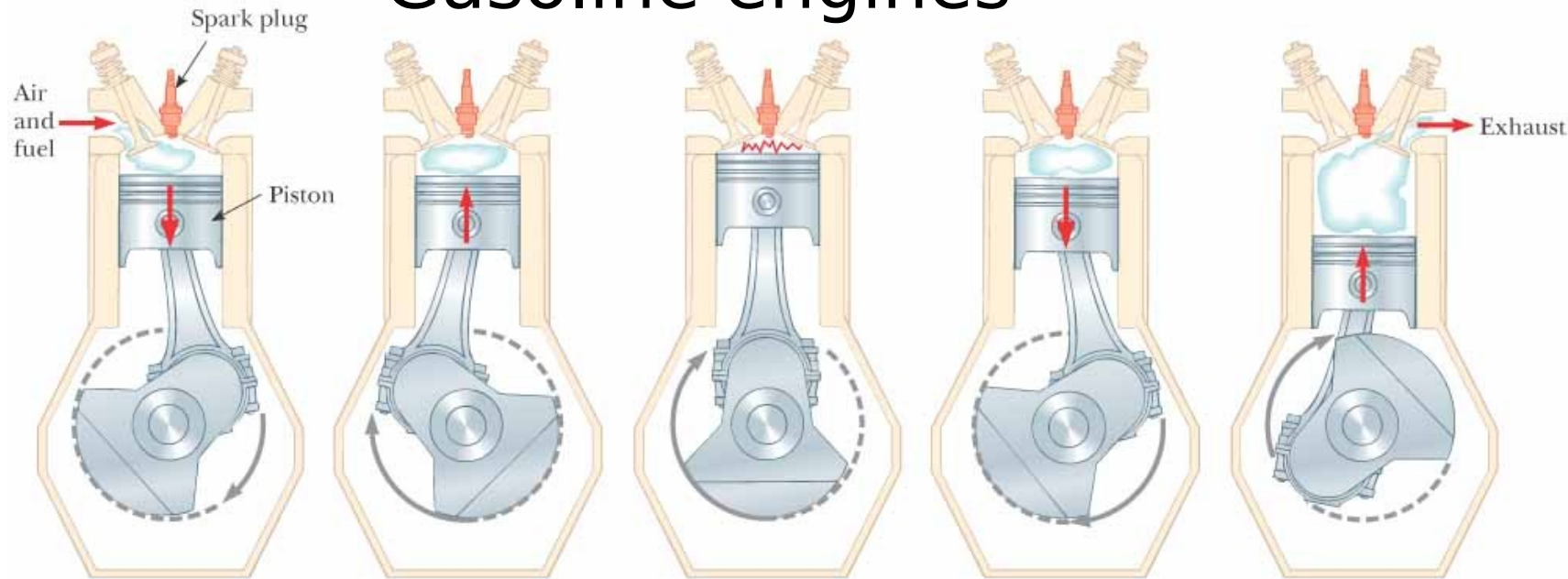
All heat engines have:
a working substance
a high-temperature reservoir
a low-temperature reservoir
a cyclical engine



Steam power plant

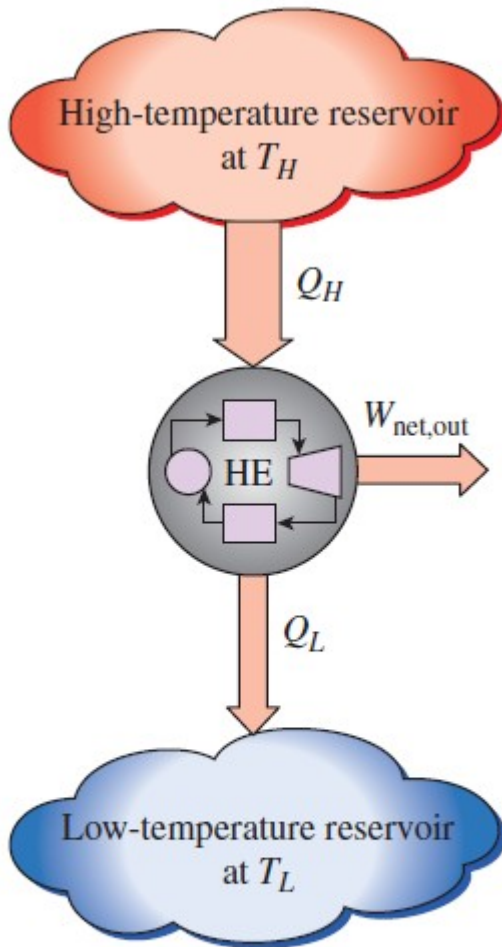


Gasoline engines



Thermal -efficiency

$$(\text{efficiency}) = \frac{(\text{desired output})}{(\text{required input})}$$

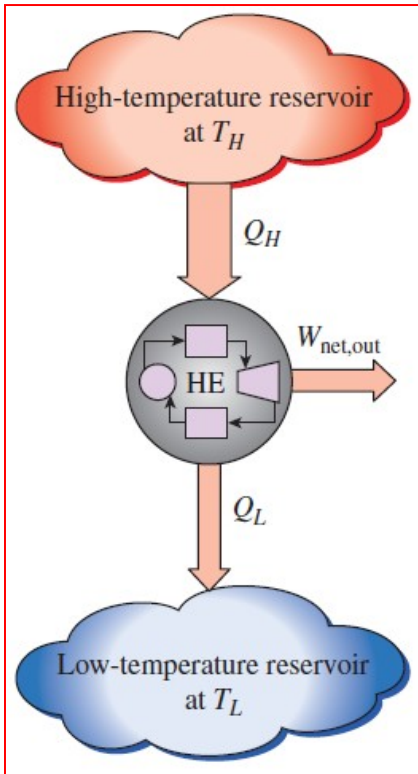


$$(\text{thermal efficiency}) = \frac{(\text{net work out})}{(\text{heat from high-temperature source})}$$

$$\eta_{\text{thermal}} = \frac{W_{\text{net out}}}{Q_H}$$

Carnot efficiency

Isolated system



Isolated system conserves energy:

$$W_{\text{net out}} = Q_H - Q_L$$

Isolated system generates entropy:

$$-\frac{Q_H}{T_H} + \frac{Q_L}{T_L} \geq 0$$

All **reversible engines** running in cycle between reservoirs of two fixed temperatures T_H and T_L have the same thermal efficiency (**Carnot efficiency**):

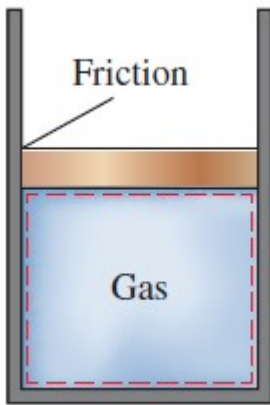
$$\frac{Q_H}{T_H} = \frac{Q_L}{T_L}, \quad \frac{W_{\text{net out}}}{Q_H} = 1 - \frac{T_L}{T_H}$$

All real engines are **irreversible**. For an irreversible (i.e. real) engine running in cycle between reservoirs of two fixed temperatures T_H and T_L , the thermal efficiency is below the Carnot efficiency:

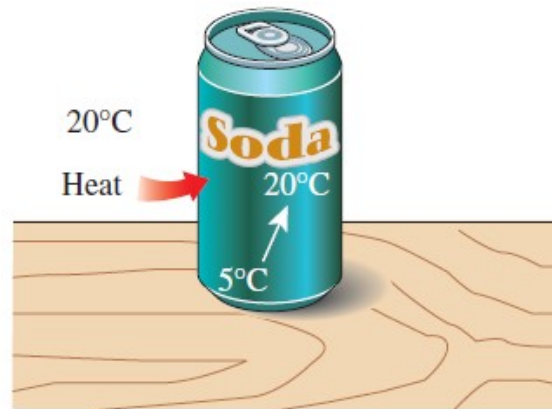
$$\frac{Q_H}{T_H} < \frac{Q_L}{T_L}, \quad \frac{W_{\text{net out}}}{Q_H} < 1 - \frac{T_L}{T_H}$$

All real processes are irreversible

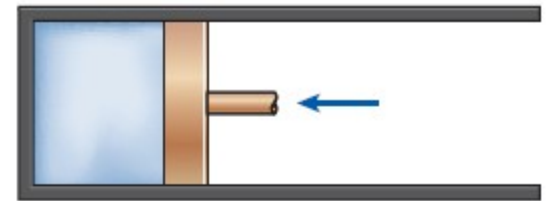
So many ways to generate entropy (i.e., to be irreversible)



Friction



Heat transfer through a temperature difference



(a) Fast compression

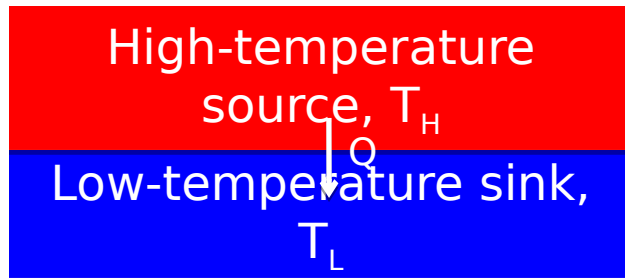


(b) Fast expansion



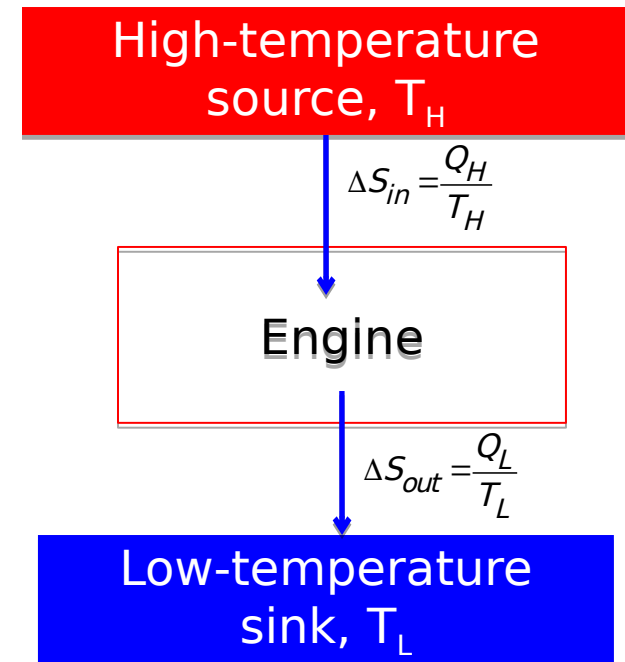
(c) Unrestrained expansion

Carnot: “The steam is here only a means of transporting the caloric.”



Thermal contact **generates** entropy
transports entropy Q

$$S_{gen} = \frac{Q}{T_L} - \frac{Q}{T_H}$$



Reversible engine

$$\frac{Q_H}{T_H} = \frac{Q_L}{T_L}$$

Carnot's analogy in his own words

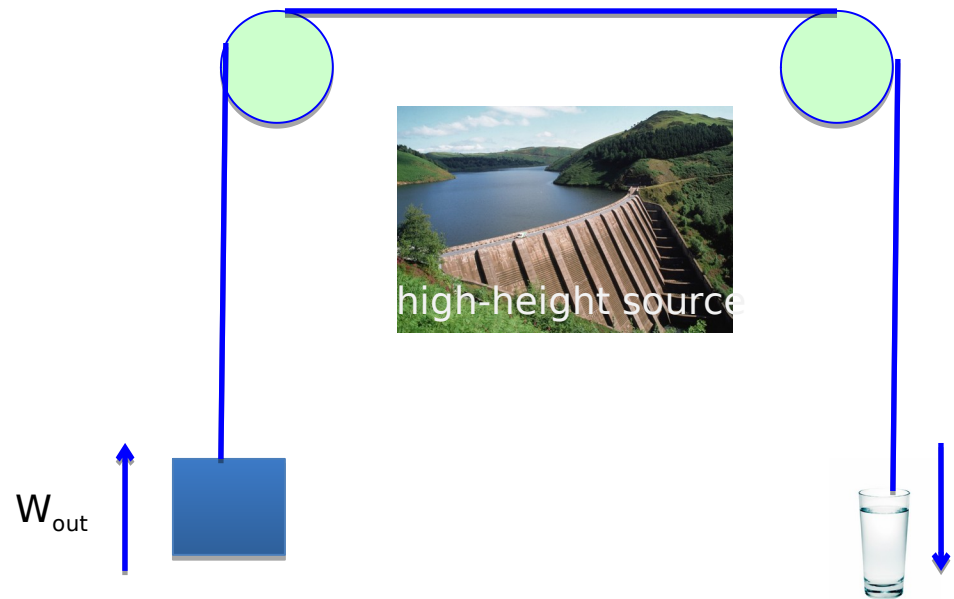
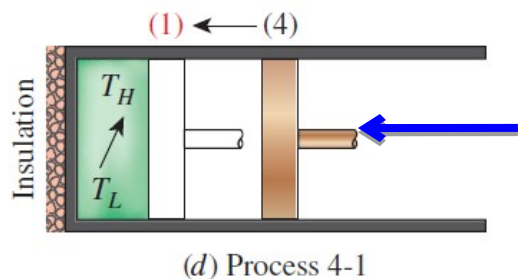
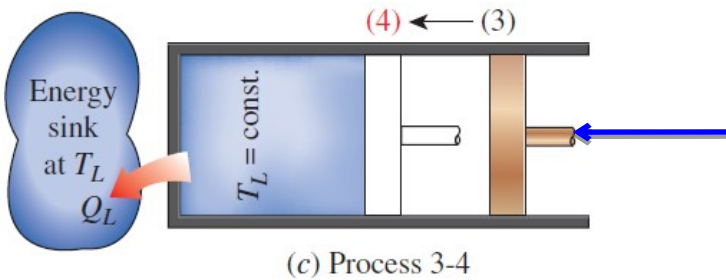
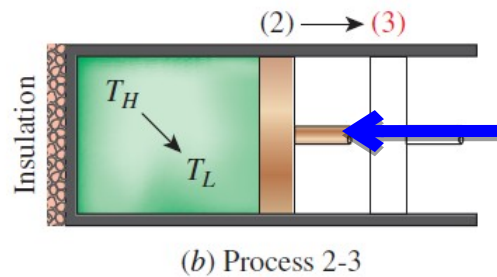
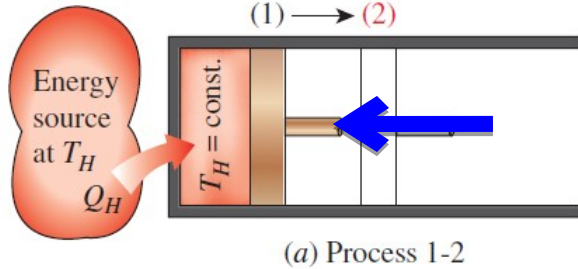
The **motive power** of a waterfall depends on its height and on the quantity of the liquid; the motive power of **heat** depends also on the quantity of **caloric** used, and on what may be termed, on what in fact we will call, the height of its fall, that is to say, the difference of temperature of the bodies between which the exchange of caloric is made. In the waterfall the motive power is exactly proportional to the difference of level between the higher and lower reservoirs. In the fall of caloric the motive power undoubtedly increases with the difference of temperature between the warm and the cold bodies; but we do not know whether it is proportional to this difference. We do not know, for example, whether the fall of caloric from 100 to 50 degrees furnishes more or less motive power than the fall of this same caloric from 50 to zero. It is a question which we propose to examine hereafter.

Modern translations

Motive power: work

Caloric: entropy

Carnot's analogy in pictures



Carnot efficiency

reversible engine running between two reservoirs of fixed temperatures T_H and T_L

Carnot efficiency:
$$\frac{W_{\text{net out}}}{Q_H} = 1 - \frac{T_L}{T_H}$$

Low-temperature reservoir is the atmosphere:

$$T_L = 300\text{K}$$

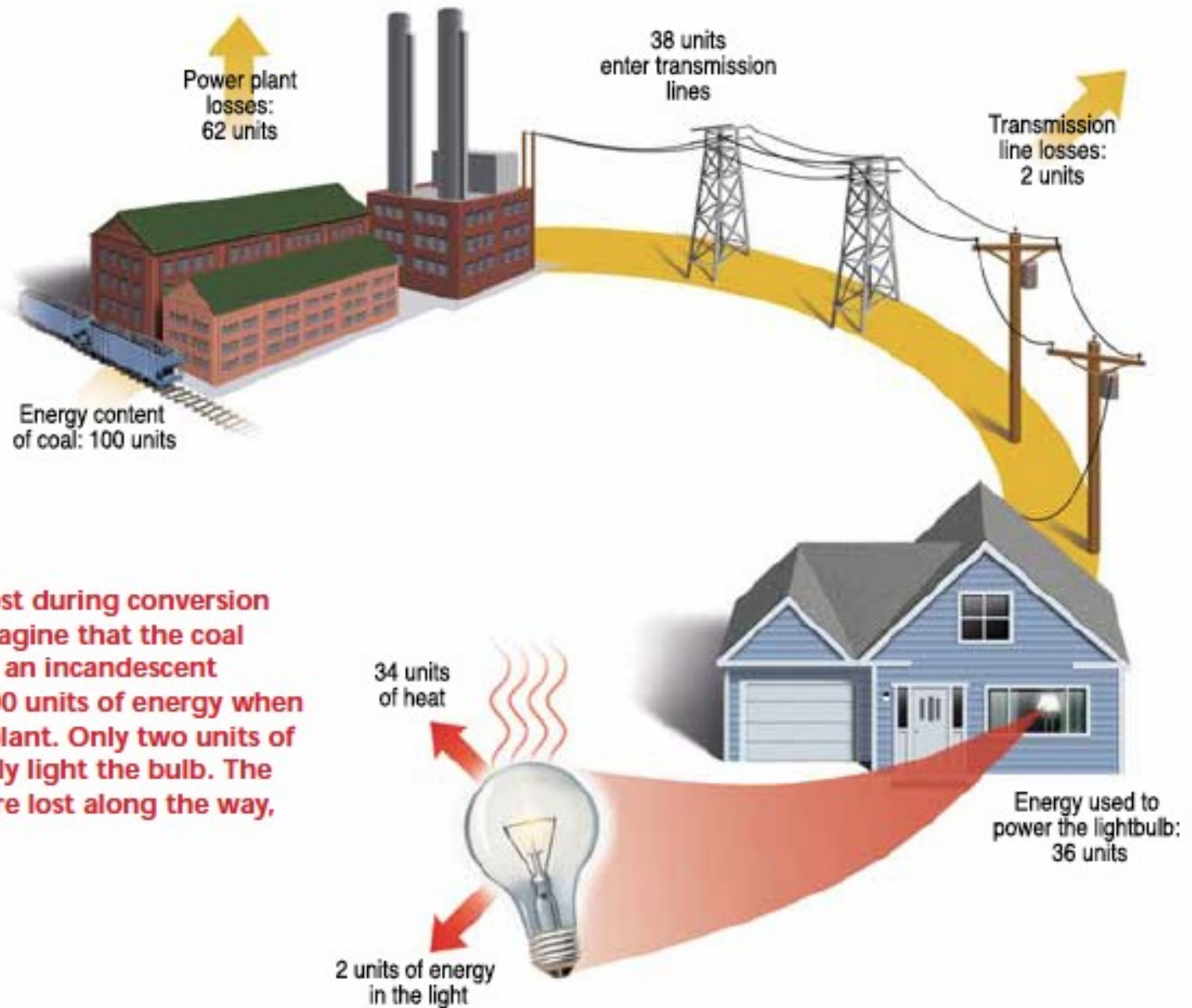
High-temperature reservoir is limited by materials

$$T_H = 600\text{K}$$

(Melting point of iron is 1811 K. Metals creep at temperatures much below the melting point.)

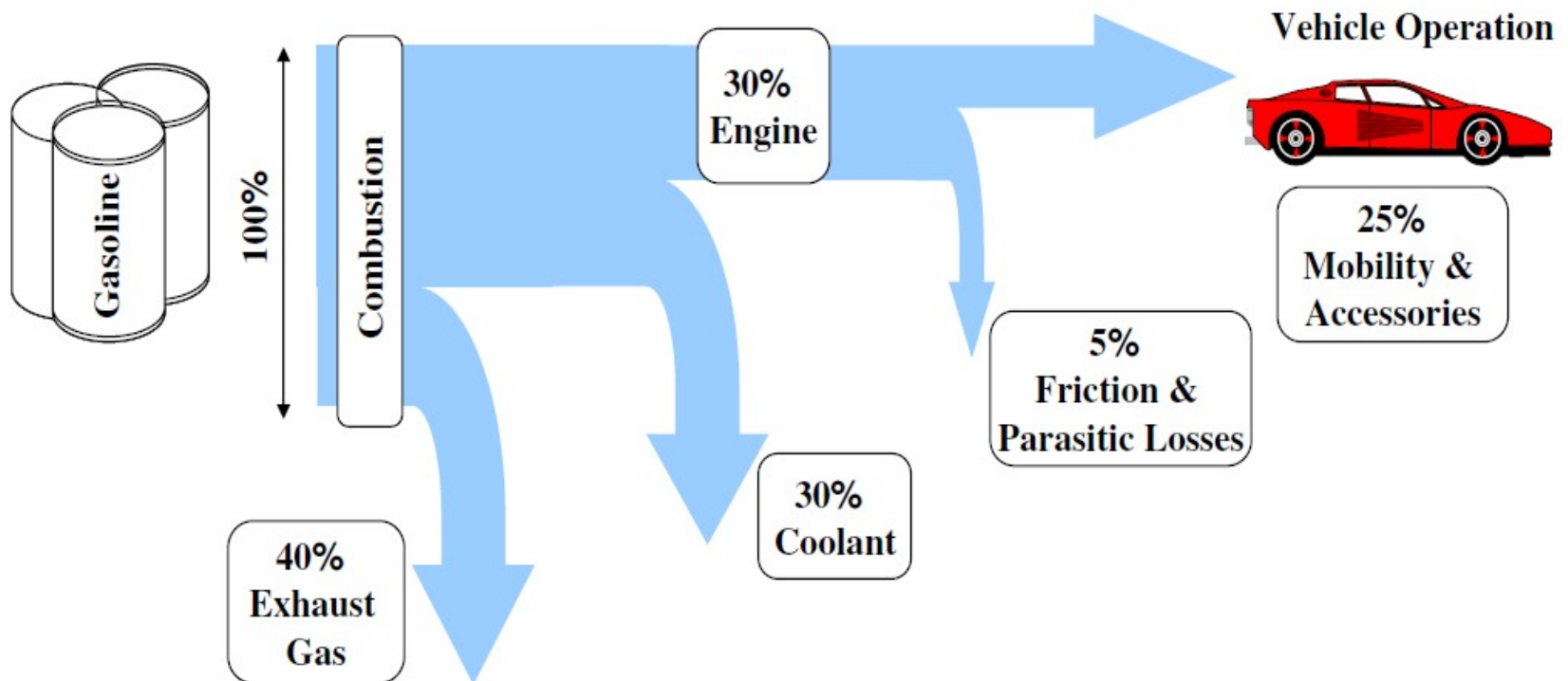
$$1 - \frac{T_L}{T_H} = 1 - \frac{300\text{K}}{600\text{K}} = 0.5$$

Carnot efficiency in numbers



Example of energy lost during conversion and transmission. Imagine that the coal needed to illuminate an incandescent lightbulb contains 100 units of energy when it enters the power plant. Only two units of that energy eventually light the bulb. The remaining 98 units are lost along the way, primarily as heat.

Wasted energy



Refrigerator

Isolated system

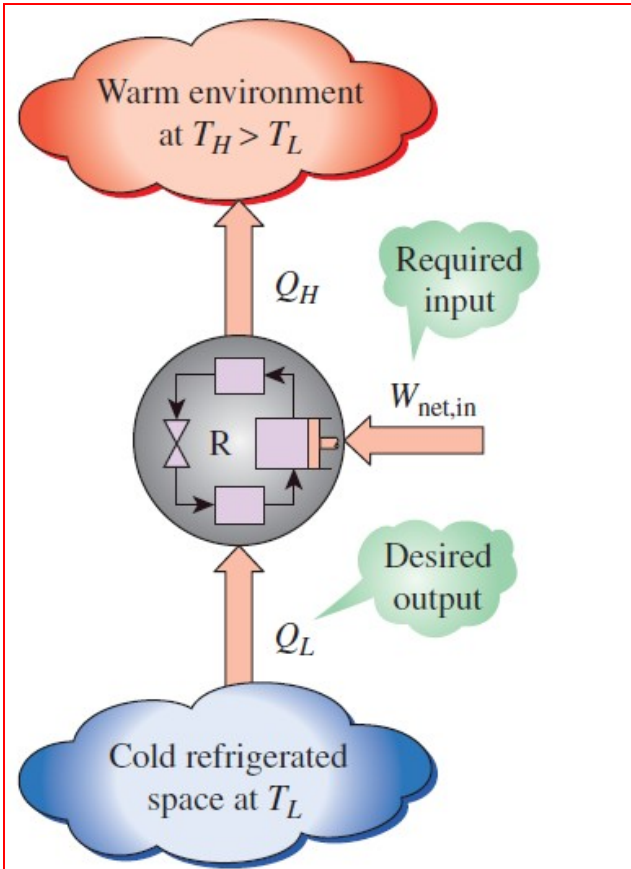


FIGURE 6–20

The objective of a refrigerator is to remove Q_L from the cooled space.

$$(\text{efficiency}) = \frac{(\text{desired output})}{(\text{required input})}$$

$$(\text{coefficient of performance, COP}) = \frac{Q_L}{W_{\text{net in}}}$$

Isolated system conserves energy:

$$W_{\text{net in}} = Q_H - Q_L$$

$$\frac{Q_H}{T_H} - \frac{Q_L}{T_L} \geq 0$$

Isolated system generates entropy:

$$\text{COP}_R \leq \frac{T_L}{T_H - T_L}$$

Carnot limit:

Isolated system

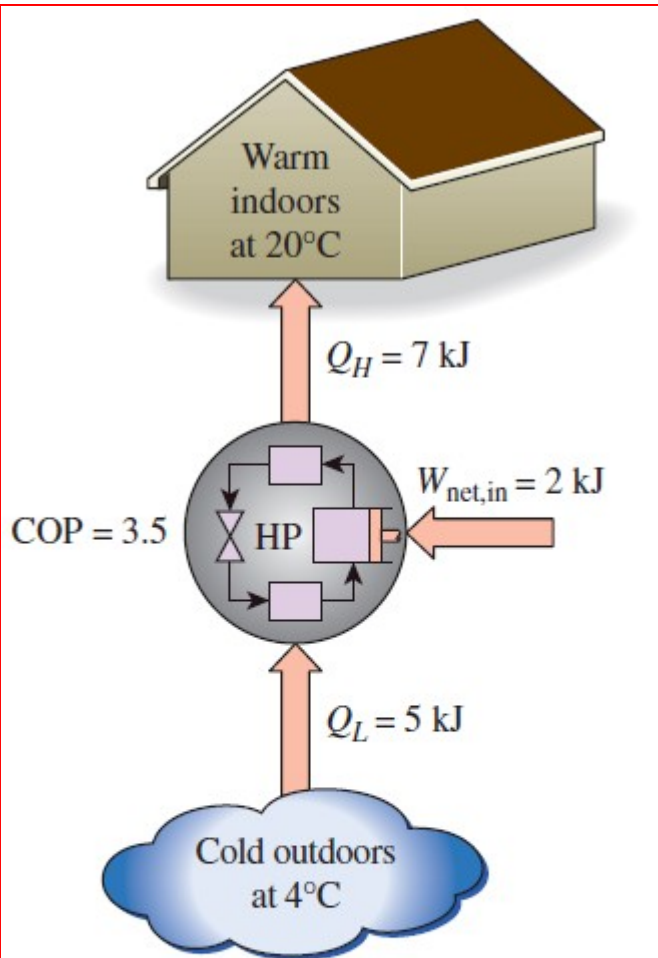


FIGURE 6–22

The work supplied to a heat pump is used to extract energy from the cold outdoors and carry it into the warm indoors.

Heat pump

$$(\text{efficiency}) = \frac{(\text{desired output})}{(\text{required input})}$$

$$(\text{coefficient of performance, COP}) = \frac{Q_H}{W_{\text{net in}}}$$

Isolated system conserves energy:

$$W_{\text{net in}} = Q_H - Q_L$$

$$\frac{Q_H}{T_H} - \frac{Q_L}{T_L} \geq 0$$

Isolated system generates entropy:

$$\text{COP}_{\text{HP}} \leq \frac{T_H}{T_H - T_L}$$

Carnot limit:

Summary

- Thermodynamics **permits** heater (a device running in cycle to convert work to heat).
- Thermodynamics **forbids** perpetual motion of the second kind (a device running in cycle to produce work by receiving heat from a **single reservoir** of a fixed temperature).
- **Carnot cycle**: A reversible cycle consisting of isothermal processes at **two temperatures** T_H and T_L , and two isentropic processes.
- All **reversible engines** running in cycle between reservoirs of two fixed temperatures T_H and T_L have the same thermal efficiency (**Carnot efficiency**):

$$\frac{W_{\text{net out}}}{Q_H} = 1 - \frac{T_L}{T_H}$$

- All real engines are **irreversible**. For an irreversible (i.e. real) engine running in cycle between reservoirs of two fixed temperatures T_H and T_L , the thermal efficiency is below the Carnot efficiency (**Carnot limit**):

$$\frac{W_{\text{net out}}}{Q_H} < 1 - \frac{T_L}{T_H}$$

- Carnot cycle also limits the coefficients of performance of **refrigerators** and **heat pumps**.

Efficiency of a Heat Engine

Assumption:

$\Delta U = 0$ for each cycle, else the engine would get hotter (or colder) with every

cycle
An amount of heat Q_h is supplied from the hot reservoir to the engine during each cycle. Of that heat, some appears as work, and the rest, Q_c , is given off as waste heat to the cold reservoir.

$$W = Q_h - Q_c$$

The efficiency is the fraction of the heat supplied to the engine that appears as work.

$$e = \frac{W}{Q_h}$$

Efficiency of a Heat Engine

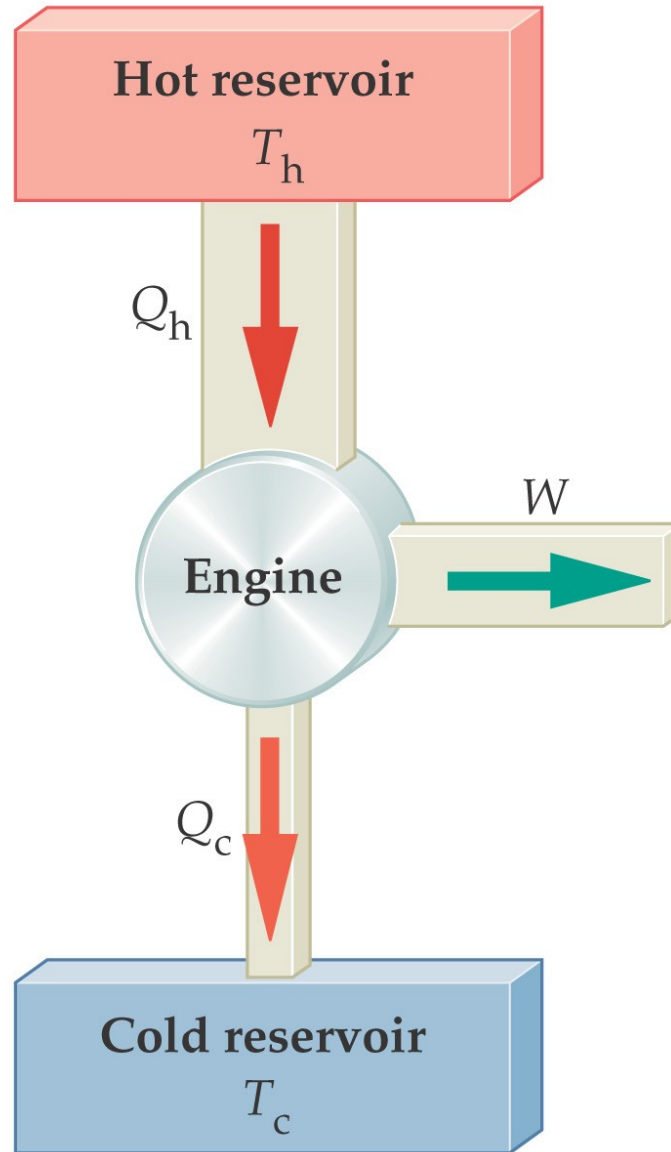
The efficiency can also be written:

Efficiency of a Heat Engine, e

$$e = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

SI unit: dimensionless

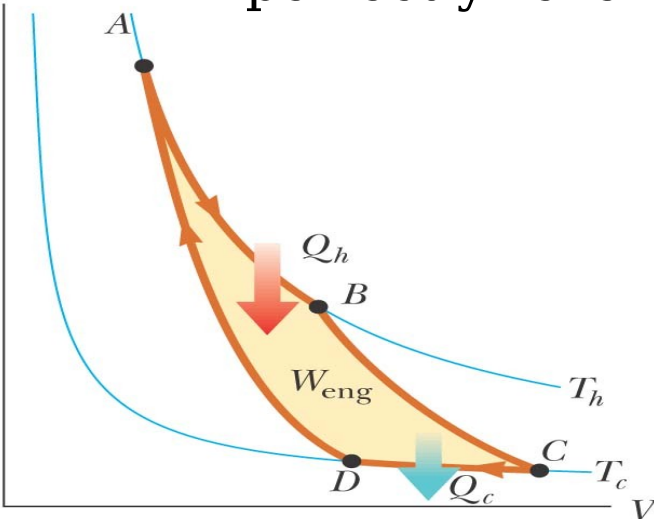
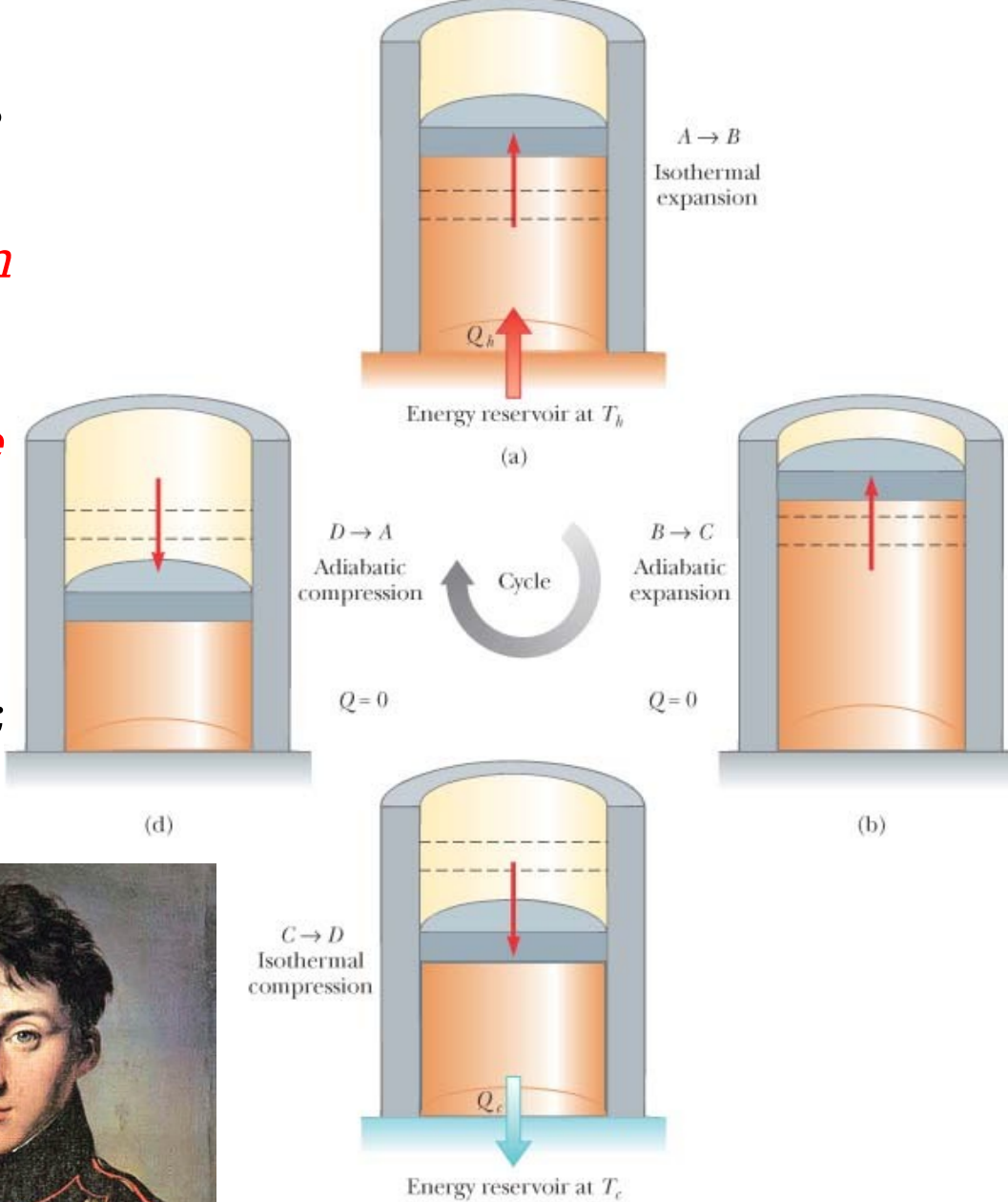
In order for the engine to run, there must be a temperature difference; otherwise heat will not be transferred.



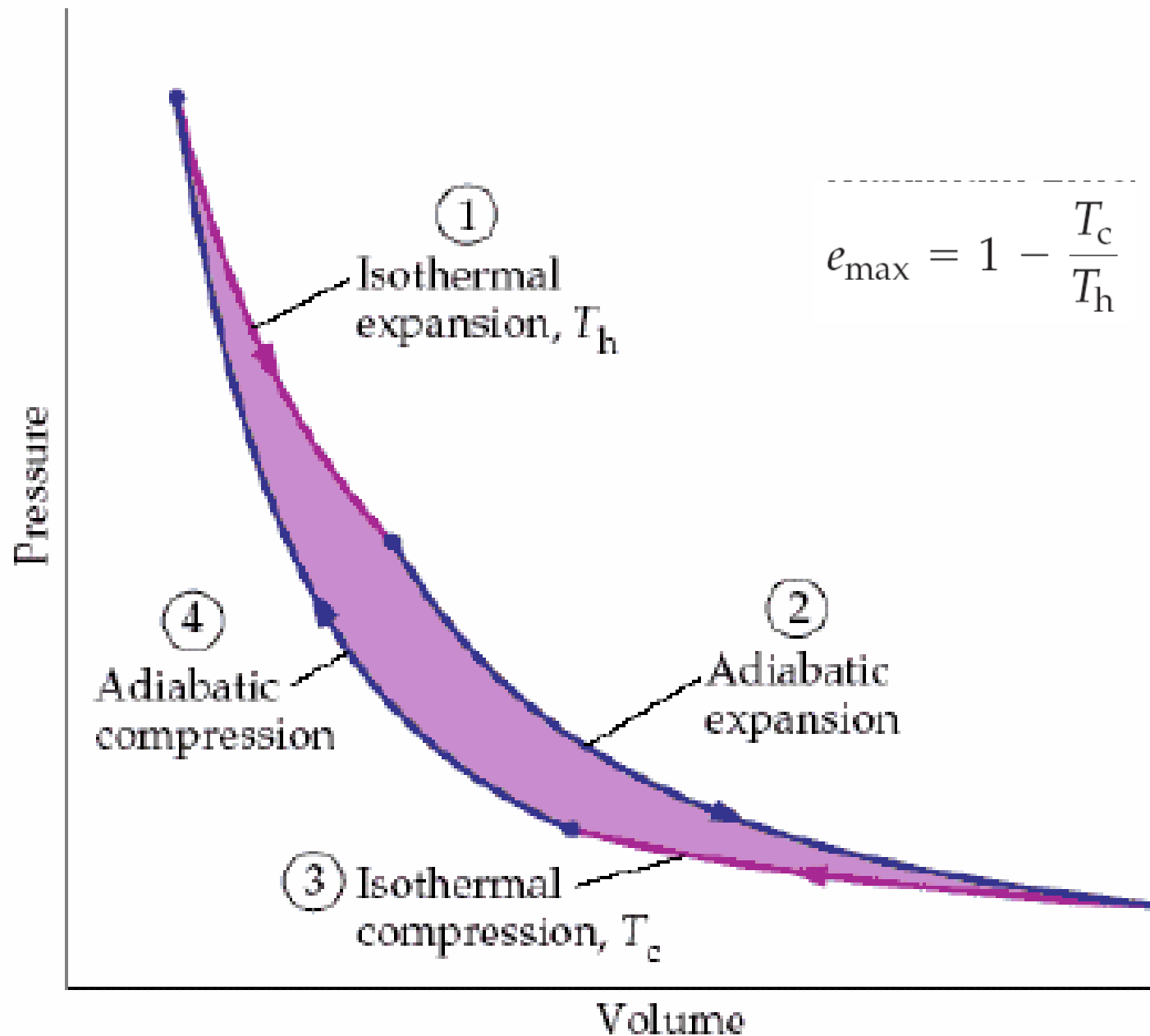
The maximum-efficiency heat engine is described in Carnot's theorem:

If an engine operating between two constant-temperature reservoirs is to have maximum efficiency, it must be an engine in which all processes are reversible. In addition, all reversible engines operating between the same two temperatures, T_c and T_h , have the same efficiency.

This is an idealization; no real engine can be perfectly reversible.



The efficiency of the Carnot Cycle:



Maximum Work from a Heat Engine Cycle

Maximum Efficiency of a Heat Engine

$$e_{\max} = 1 - \frac{T_c}{T_h}$$

The maximum work a heat engine can do is then:

$$W_{\max} = e_{\max} Q_h = \left(1 - \frac{T_c}{T_h}\right) Q_h$$

If the two reservoirs are at the same temperature, the efficiency is zero.

The smaller the ratio of the cold temperature to the hot temperature, the closer the efficiency will be to 1.

Approaching absolute zero

The efficiency of a **reversible** engine:

$$1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h}$$

So a reversible engine has the following relation between the heat transferred and the reservoir temperatures:

$$\frac{Q_c}{Q_h} = \frac{T_c}{T_h}$$

(irreversible engines

so... how cold can we make something?

$$\frac{Q_c}{Q_h} < \frac{T_c}{T_h}$$

**As a system approaches absolute zero,
heat becomes harder to extract**

The Laws of Thermodynamics

I) $\Delta U = Q - W$

A continuous system (which is not consuming internal energy) cannot output more work than it takes in heat energy

→ **YOU CAN'T WIN!**

II) **Maximum Efficiency of a Heat Engine**

$$e_{\max} = 1 - \frac{T_c}{T_h}$$

III) $T_c = 0$ is not achievable

→ **YOU CAN'T BREAK EVEN!**



Entropy

A reversible engine has the following relation between the heat transferred and the reservoir temperatures:

$$\frac{Q_c}{Q_h} = \frac{T_c}{T_h}$$

Rewriting,

$$\frac{Q_c}{T_c} = \frac{Q_h}{T_h}$$

This quantity, Q/T , is the same for both reservoirs. This conserved quantity is defined as the **change in entropy**.

Entropy

Definition of Entropy Change, ΔS

$$\Delta S = \frac{Q}{T}$$

SI unit: J/K

Like internal energy, entropy is a state function

Unlike energy, entropy is NOT conserved

In a reversible heat engine,
the entropy does not
change.

Entropy

A real engine will operate at a lower efficiency than a reversible engine; this means that less heat is converted to work.

$$1 - \frac{Q_c}{Q_h} < 1 - \frac{T_c}{T_h}$$

$$\frac{Q_c}{T_c} > \frac{Q_h}{T_h}$$

$$\Delta S_{\text{total}} = -\frac{Q_h}{T_h} + \frac{Q_c}{T_c} > 0 \quad \text{for irreversible processes}$$

Any irreversible process results
in an increase of entropy.

Entropy

To generalize:

- The total entropy of the universe increases whenever an irreversible process occurs.
- The total entropy of the universe is unchanged whenever a reversible process occurs.

Since all real processes are irreversible, the entropy of the universe continually increases. If entropy decreases in a system due to work being done on it, a greater increase in entropy occurs outside the system.

Order, Disorder, and Entropy

Entropy can be thought of as the increase in disorder in the universe.

In this diagram, the end state is less ordered than the initial state – the separation between low and high temperature areas has been lost.

